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Numerous examples of the carbene character of atomic carbon produced in a low intensity arc under high vacuum have recently been reported from this laboratory.

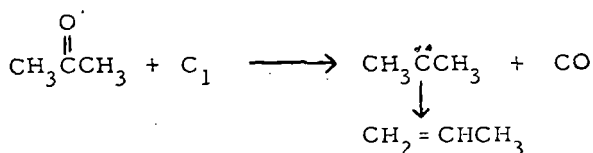
In an effort to find reactions of atomic carbon which might not be classified as normal carbene processes, the reactions of atomic carbon with carbonyl compounds were studied. The reaction of carbon atoms with acetone cocondensed on a liquid nitrogen cooled surface produced carbon monoxide and propylene in good yield (see Table I).

Table I

<u>Compound</u>	<u>Yield^a</u>
CO	59.6%
CH ₂ = CHCH ₃	54.2%

^a calculated as Mm product/MmC₁ vaporized

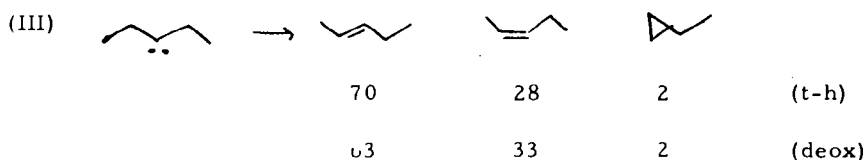
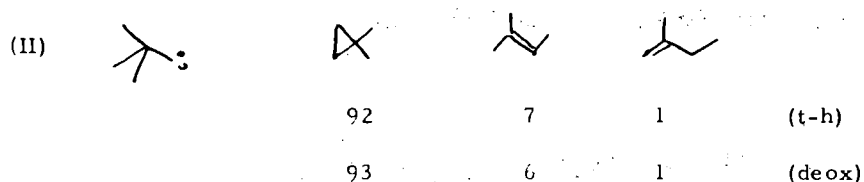
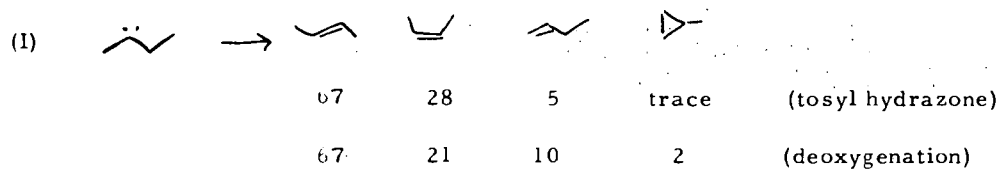
The production of Carbon monoxide and propylene in nearly equal amounts suggested the following reaction sequence:



If this scheme were operative, the reaction was novel deoxygenation process to produce the subvalent carbene species and would thus provide an opportunity to generate a wide variety of carbenes at low temperatures. To test the proposed scheme, the reaction of acetone with C¹⁴ enriched electrodes was examined. As

This method was found to be a general preparation of alkyl carbenes and the data gathered on product distribution from the deoxygenation method closely resemble those from tosyl hydrazone decompositions.

Three such comparisons are given below:



Thus, it appears that deoxygenation produces an intermediate very similar to the process generally assumed to be a carbene preparation. It is quite striking that the similarities between reaction at a liquid nitrogen cooled surface and a decomposition performed at $\sim 160^\circ$ are so great. We feel this indicates a low activation energy for the intramolecular, carbene reactions.

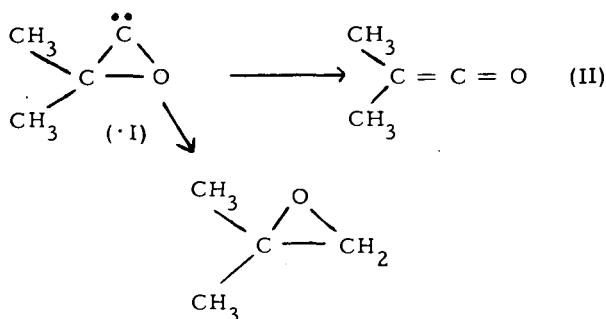
Deoxygenation was extended to other materials. It was observed that propylene oxide deoxygenated to propylene and carbon monoxide:

From the above data, we feel that oxygen abstraction is a convenient method for the generation of carbenes and radicals, free of complexing at low temperatures.

would be expected from the scheme, the propylene gave a molar activity 0.039 while the Carbon monoxide was found have a molar activity 0.91. This established that Carbon monoxide did indeed arise from a deoxygenation process involving C_1 and that the propylene was formed in a process not involving carbon from the electrodes.

As a second check, the reaction forming propylene should also be intramolecular if a carbene were involved since simple hydrogen transfer is all that is required for product formation. A mixture of acetone $d_6/d_o = 1.25$ was subjected to the reaction conditions and the resultant propylene analyzed by mass spectroscopy. The ratio propylene $d_6/d_o = 1.32$, confirming the intramolecular character of the process.

The dimer of the carbene, 2,3-dimethyl-2-butene, was not observed. This may be attributed to the relative rapidity of hydrogen transfer as opposed to the rate of diffusion of dimethyl carbene through the acetone matrix. It also appears that the process of Carbon atom insertion into carbon-carbon double bonds does not take place into carbonyl functions since such an adduct (I) would be expected to give either dimethyl ketene (II) or isobutylene oxide (III).



Neither of these products were formed.